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Removal of mercury from aqueous solution using sheep bone charcoal

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Abstract

The carbon derived from sheep bone with zinc chloride activation was applied for the adsorption of mercury (II). The effect of solution temperature, adsorption time, pH value and initial concentration of mercury(II) ions on the adsorption ability was investigated in a bfigatch process mode. The morphology and structure were characterized by scanning electron microscopy and X-ray diffraction. The BET surface area and pore volume of the prepared sheep bone charcoal were 83.98 m^2/g and 0.246 cm^3/g, respectively. The equilibrium data were fitted to linear and Freundlich isotherm.

Key words: Sheep bone charcoal; Removal of mercury; Static adsorption; Isotherms; Pore structure

1. Introduction

Recently, heavy metal compounds in wastewater from high industry activities have caused environmental pollution and serious symptoms of poisoning. Heavy metal pollution caused by cadmium, chromium, copper, lead, mercury, nickel and arsenic is most serious to the human body [1]. Mercury is carcinogenic, mutagenic, teratogenic and promotes tyrosinemia. Especially, high-concentration of mercury is associated strongly with impairment of pulmonary and kidney function, chest pain and dyspnousea [2]. The illness, which came to be known as Minamata disease, is caused by mercury poisoning as a result of eating contaminated fish [3].Mercury has very high tendency for binding to proteins and it mainly affects the renal and nervous systems [4].In humans, the initial symptoms include numbness of the lips and limbs. As the sickness progresses, permanent damage is done to the central nervous system.

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Because of the above reasons, mercury must be removed to very low levels from wastewater generated in industries such as metal smelting and caustic-chlorine production in mercury cells, metal processing, plating and metal finishing [5]. Numerous physical and chemical separation processes, such as solvent extraction, ion-exchange, precipitation, membrane separation, reverse osmosis, coagulation and photoreduction [6-9], have been applied for effective reducing of mercury concentrations from various aqueous solutions. However, most of these methods require either high-energy or large quantities of chemicals. Accordingly, adsorption is used as another facile, effective technique for mercury removal from wastewater. Among various adsorption agents, activated carbons are considered to be very high-effective, but it is expensive for large-scale application [10]. Much effort is devoted to the study on low-cost adsorbents [11-13]. For instance, camel bone charcoal obtained from camel bone is used as an adsorbent for the removal of Hg(II) from wastewater effluents by Egypt researchers Saad S.M. Hassan, Awaad H.A. Aboterik [14]. Hierarchical porous carbon obtained from animal bone by China researchers Wentao Huang et al.[15]. The accumulation of the bone increases day by day, much of attention was paid to the carbonization of bone char. The utilization of this bone for bone charcoal synthesis may give a solution to solid waste management in some industries by using these wastes for removal of pollutants [14].

In this study, as a utilization of waste materials, the carbonous material from sheep bone is prepared and activated using zinc oxide. Also, its adsorption performance to Hg (Ⅱ) was evaluated. These studies provide the favorable scientific basis to the comprehensive development of solid waste, and offer the useful theoretical data to purification treatment of wastewater contain the Hg (Ⅱ).

2. Experimental

2.1. Materials and methods

2.1.1. Adsorbent

Discard sheep bone char (BC) residue from Dolan restaurant in Urumqi (China), were tested. Bones were cleaned from meat and fat and then washed with tap water several times. Then, they were transferred to an oven and dried at 393 K for 12 h. Dried bones were crushed and milled into bone particles of 0.38-0.83 mm. 10 g of the sample was impregnated into $ZnCl_2$ solutions under stirring, and left to stand for another 12 h. The bone precipitates were rinsed repeatedly, and vacuum-dried at 120 ℃ for 12 h. Finally, activated carbonous materials were produced by the pyrolysis of the precipitates at 400℃for 40 min and the activation at 800℃ for 40 min under inert atmosphere. A schematic set-up showing the reactor and flow processes is illustrated in Fig. 1. The as-prepared carbon was washed with 1M HCl solution, distilled water till pH value above 6, and vacuum-dried at 120℃ for 12h. Bone char (CBC) residues are the result of a pyrolysis process according to the following conditions:

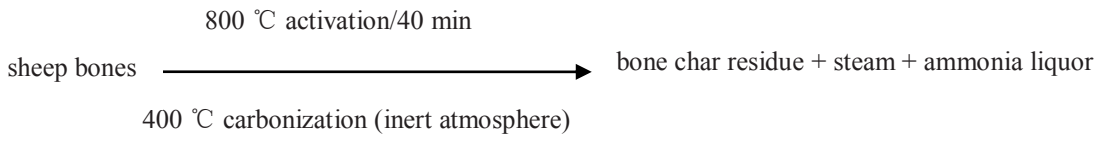

Fig. 1. Setup for obtain activated carbon from sheep bone.

2.1.2. Characterization

The morphology and structure of the adsorbent were conducted on a Scanning Electron Microscopy (SEM , LEO-l430VP) and The surface area and pore volume of bone charcoal were determined by nitrogen adsorption isotherms BET .

2.2. Procedure

2.2.1. Sorption experiments

A stock Hg(II) nitrate (1000 mg/L) standard solution was prepared by dissolving the $HgCl_2$ heavy metal salt. A working solutions (50-600 mg/L) were prepared by dilution with deionized distilled water.

Batch sorption experiments were conducted by using 80 mg/L of Hg(II). The solutions were adjusted to pH 1–9 using 0.1N of either nitric acid or sodium hydroxide solution and placed in 250 mL reagent bottles. 25 mL of metal ion solutions were pipetted into the test bottles. A known quantity 0.1 g of sheep bone charcoal was added to each bottle. The solutions were agitated at a speed of 150 rpm for 0.5–6 h at 25± 1℃in a shaking incubator. The bone charcoal was separated by filtration and mercury(II) content of the filtrate was determined using atomic fluorescence spectrometry. The adsorptive capacity (q_e) was calculated according to the following equation:

$$q_e = \frac{(c_0 - c_e) \times V}{m} \quad (1)$$

where m is the mass of adsorbent used (g), V is the total volume of mercury (II) solution (mL), C_0 is the initial concentration of mercury(II) solution (mg/L), and C_e is the residual mercury(II) concentration (mg/L).

The linear model, which describes the accumulation of solute by sorbent as directly proportional to the solution concentration is presented by the relation:

$$q_e = K_D C_e \quad (2)$$

The constant of proportionality or distribution coefficient K_D is often referred to as the partition coefficient.

The Langmuir model represents one of the first theoretical treatments of non-linear sorption, and has

been successfully applied to a wide range of systems that exhibit limiting or maximum sorption capacities. The model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate in the plane of the surface.

The Langmuir isotherm is given by:

$$q_e = \frac{Q^0 b C_e}{1 + b C_e} \tag{3}$$

where Q^0 and b are Langmuir constants related to adsorption capacity and energy of adsorption, respectively [16] . Eq. (3) is usually linearized by inversion to obtain the following form:

$$\frac{1}{q_e} = \frac{1}{Q^0} + \frac{1}{bQ^0}\frac{1}{C_e} \tag{4}$$

Eq. (3) is equally used to analyze batch equilibrium data by plotting $1/q_e$ versus $1/ C_e$, which yields a linear plot if the data conform to the Langmuir isotherm.

The Freundlich isotherm is the most widely used non-linear sorption model and is given by the general form:

$$q_e = K_F C_e^{1/n} \tag{5}$$

where K_F relates to sorption capacity and n to sorption intensity.

The logarithmic form of Eq. (5) given below is usually used to fit data from batch equilibrium studies[8]:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{6}$$

3. Experimental

3.1. Effect of solution temperature on adsorption

Fig. 2 shows the removal of mercury(II) as a function of solution temperature in an aqueous solution of pH 3. The initial Hg(II) concentration is 80 mg/L and adsorbent dosage is 0.1g. With varying the temperature of Hg(II) solution from 25 to 65 ℃, the adsorption efficiency decreased. The decrease in adsorption efficiency indicates an exothermic process. This may be due to the increasing trend to desorp mercury(II) from the interface to the solution or the distorted active sites on adsorbent. The optimum solution temperature was selected as 25 ℃ for sheep bone char.

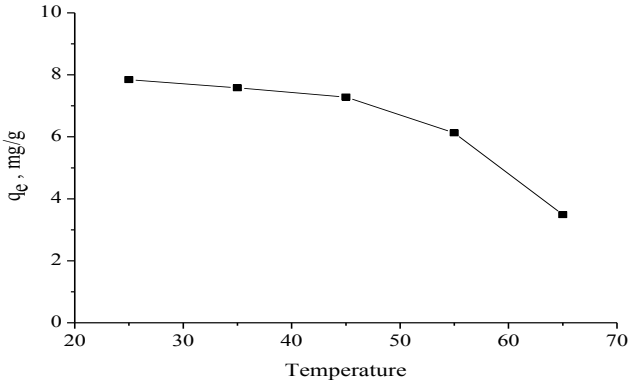

Fig. 2. Effect of solution temperature on Hg(II) removal.

3.2. Effect of contact time on adsorption

Fig. 3 shows the effect of contact time on the removal of mercury(II) by sheep bone charcoal. Adsorbent dosage of 0.1 g and solution temperature of 25℃. As seen here, mercury sorption capacity increases with the time during the first 120 min and attains equilibrium then decreases.

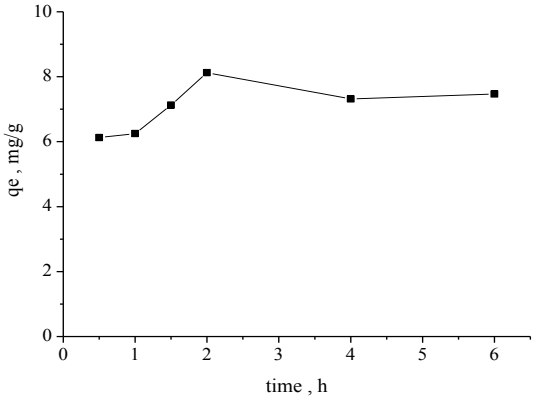

Fig. 3. Effect of contact time on Hg(II) removal .

3.3. Effect of pH on adsorption

The effect of pH on Hg(II) adsorption was studied with the pH range adjusted to around 1–9 (Fig. 4) as adsorbent dosage of 0.1 g and solution temperature of 25 ℃. At pH values below 2, hydrogen ions are likely to compete with mercuric ions and at pH values above 7 mercuric ions might precipitate. It is noticed that the adsorption decreased with the increase of pH value, the maximum adsorption was observed at pH 3.0. In general the results indicated that the adsorption is highly pH dependent. Similar results have been reported in previous studies[17] .

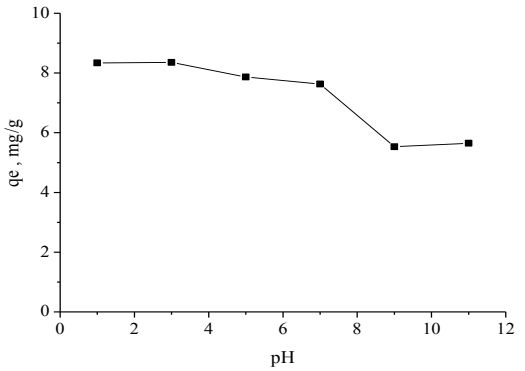

Fig. 4. Effect of pH on Hg(II) removal .

3.4. Effect of Hg^{2+} concentration on adsorption

Fig. 5 shows the effects of Hg^{2+} concentration onto the sorption capacity as solution of pH 3, solution temperature of 25 ℃ and adsorbent dosage of 0.1g. It was found that the maximum adsorption

Hg^{2+}sorption capacity was observed at 400mg/L .

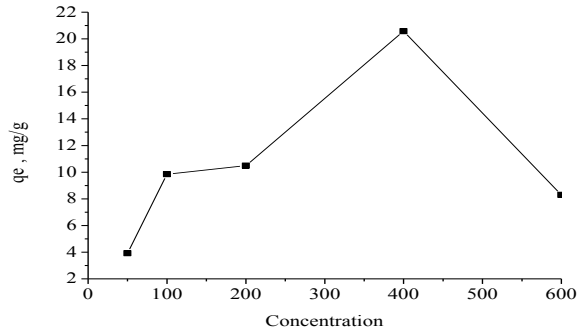

Fig. 5. Effect of initial concentration on Hg(II) removal .

3.5 Adsorption isotherms

The linear, Langmuir and Freundlich isotherms relate metal uptake per unit weight of the adsorbent q_e to the equilibrium adsorbate concentration in the bulk fluid phase Ce. Eqs. (2),(4) and (6) are used for the analysis of equilibrium batch experiment data linear, Langmuir and Freundlich isotherms, respectively[8]. Figs. 6–8 present the linear, Langmuir and Freundlich isotherm plots of mercury(II) adsorption on sheep bone charcoal.

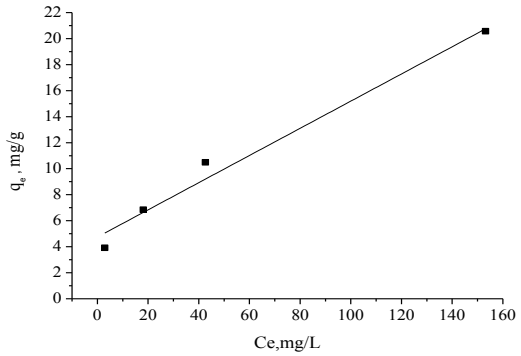

Fig. 6. Linear isotherm plot of mercury(II).

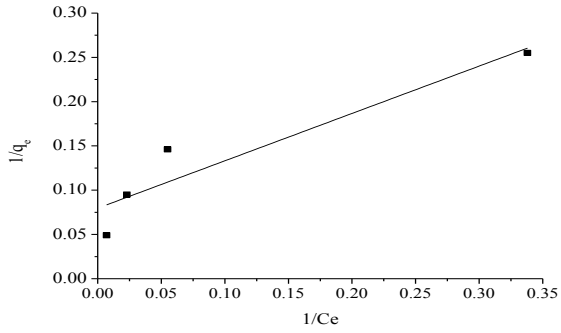

Fig.7. Langmuir isotherm plot of mercury(II) adsorption on sheep bone.

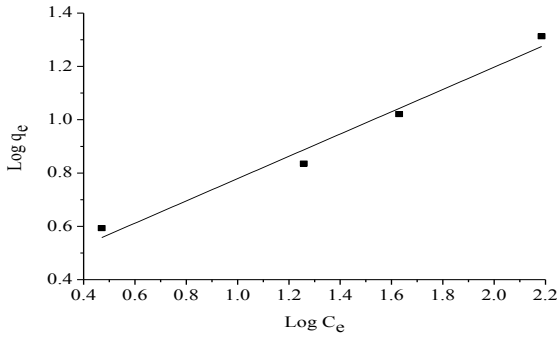

Fig. 8. Freundlich isotherm plot of mercury(II) .adsorption on sheep bone charcoal.

The equilibrium data are fitted well to Freundlich isotherm. Calculation of the isotherm parameters using these plots gives the data presented in Table 1.

Table 1. Isotherm parameters of mercury(II) adsorption on sheep bone charcoal.

Linear	Langmuir			Freundlich		
K_D(mg/L)	Q^0(mg /g)	b(mg/L)	R^2	K_F	1/n	R^2
2.61	12.550	0.149	0.8350	2.280	0.4181	0.9682

3.5. Scanning electron micrographs of sheep bone charcoal

After the activation process, carbon morphology changed and the external surface images of activated carbon obtained from scanning electron micrographs (SEM) so show. Fig. 9 (A) presents a SEM micrograph of bone char not activated. That image does not show porosity; The Fig. 9 (B) presents a SEM image after activated. The adsorbent's surface was broken, pores were created.

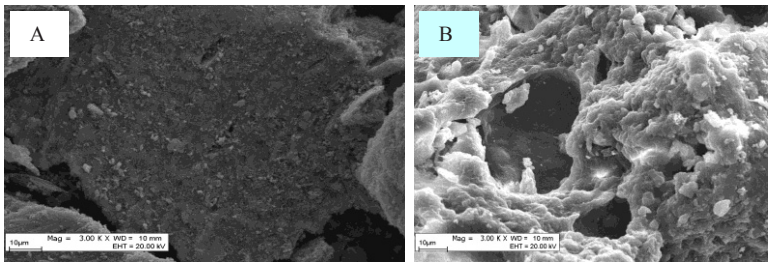

Fig. 9. (A) Non-activated sheep bone SEM micrograph, (B) sheep bone charcoal SEM micrograph.

3.6. BET surface areas of activated carbons

The surface area and pore volume of bone charcoal were determined by nitrogen adsorption isotherms at 77 K. The surface area was determined by applying the isothermal Brunauer–Emmett–Teller (BET) and total pore volume was estimated by the volume of nitrogen adsorbed at a high relative

pressure[18].The DR-method was applied to determine the volume and surface area of micropores.Table 2 reports the textural parameters obtained from N_2 adsorption isotherms. The nitrogen adsorption–desorption isotherm and the corresponding DFT (density functional theory) pore size distribution curve of the sheep bone charcoal were shown in Fig. 10. It can be seen from Fig. 10(A) that the isotherm of the sheep bone charcoal taken up a shape of type IV (according to IUPAC classification). The bone charcoal displayed more increment in nitrogen adsorption capacity at the entire relative pressure region, which suggested that additional pores were created and some small pores were widen by chemical activation [19, 20]. It can be seen in Fig. 10(B) that bone charcoal has a hierarchical pore size distribution.

Table 2. Textural parameters deduced from N_2 adsorption isotherms at 77 K for the sheep bone charcoal.

sample	S_{BET}	Vt	D
	(m^2/g)	(cm^3/g)	(nm)
sheep bone charcoal	83.98	0.246	15.39

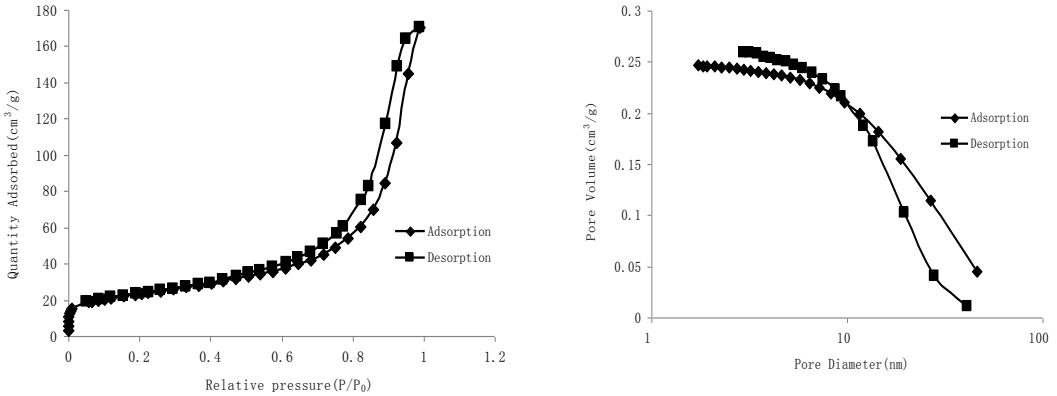

Fig. 10. (A) N2 adsorption–desorption isotherm at 77 K on bone charcoal, (B) Pore volume distribution for bone charcoal.

4. Conclusion

The adsorption capacity of mercury ions by activated carbons, sheep bone charcoal, was investigated in this study. Sheep bone charcoal was a suitable adsorbent for the removal of Hg(II) from aqueous solution. The adsorption was found to be strongly dependent on temperature, pH, and contact time. Removal of mercury from 25 mL of 80 mg/L of Hg(II) was achieved by 0.1 g of sheep bone charcoal , solution temperature 25℃, 2 hour of contact time at pH 2. Equilibrium sorption isotherm studies showed that the Freundlich isotherm model satisfactorily described the sorption data.

Acknowledgements

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